[Contribution from the Polytechnic Institute of Brooklyn]

X-Ray Investigation of Crystalline Cyclopentane and Neohexane[1]

By Benjamin Post, Robert S. Schwartz and I. Fankuchen

Thermal data indicate that crystalline cyclopentane and neohexane, both of which undergo transitions in the solid state, are highly disordered above the temperatures of the transitions. In this investigation the nature of the disorder has been studied using single crystal X-ray diffraction techniques. Between the temperature of the upper transition and the melting point, crystals of cyclopentane are hexagonal, and contain two molecules per unit cell with the molecules in close packed positions. In the same temperature range neohexane crystals are cubic, and contain four molecules per unit cell with the molecules in face-centered positions. The symmetries of the crystals and the intensities of the reflections indicate that molecules of cyclopentane, and probably neohexane, are freely rotating (or randomly oriented) in the solid, with spherical symmetry on the average.

Introduction

A number of molecular crystals exhibit transitions which result in an increase in crystal symmetry above the transition temperatures. The specific heat curves of crystalline cyclopentane and neohexane[2] show two such transitions. The temperatures and entropies of the transitions and the melting points of the crystals are shown in Table I.

Table I

Temperatures and Entropies of Transition and Fusion of Cyclopentane and Neohexane

	Cyclopentane[3]		Neohexane[4]	
	T, °C.	ΔS, e.u./mole	T, °C.	ΔS, e.u./mole
Transition I	−150.8	9.520	−146.4	10.166
Transition II	−135.1	0.600	−132.3	0.480
Fusion	− 93.4	0.802	− 99.0	0.795

It is evident from the high entropies of transition and the extremely low entropies of fusion that the crystal structures of both substances are highly disordered above the transition temperatures.[4] In this paper are presented the results of an X-ray diffraction investigation of the crystal forms which are stable between Transitions II and the melting points.

I. Cyclopentane

Experimental.—The low temperature X-ray camera and the auxiliary apparatus used in this investigation are described in detail elsewhere.[5] The technique employed involved sealing the specimen in a thin-walled glass capillary, mounting it on the goniometer arcs of a single crystal X-ray camera and freezing it in a cold gas stream. Single crystals were grown by repeatedly melting sections of the solid specimen in the capillary and slowly refreezing. Observations of crystal growth and alignment of crystals for rotation about crystallographic directions were made with the aid of a polarizing microscope mounted on the X-ray camera track.

In this way cylindrical single crystals of cyclopentane, less than 0.4 mm. in diameter, were grown. Examination with the polarizing microscope indicated that the crystals were uniaxial above Transition II; below the temperature of the transition a change occurred to a polycrystalline form of apparently lower symmetry. Sets of oscillation diagrams were taken about the c- and a-axes.

Filtered copper radiation was used; camera radius was 5.0 cm. Intensities of reflections were estimated visually, using multiple film techniques.[6] Relative values of F_{hkl}, computed from intensities after correction for Lorentz and polarization factors, are listed below in Table II under $F_{obs.}$ Crystal diameters were less than one-fifth of the optimum specimen thickness in all cases and therefore no absorption corrections were applied.

Table II

Observed and Computed Structure Factors

			$F_{calc.}$	
$hk{\cdot}l$	$F_{obs.}$	$F_{calc.}$ Free spherical rotation	Free cylindrical rotation	3-Fold orientational disorder
10.0	5.5	− 5.8	4.7	4.1
00.2	10.0	−10.0	5.5	4.2
10.1	6.9	− 7.5	6.6	5.3
10.2	1.3	+ 1.9	4.2	2.2
11.0	1.0	+ 0.9	2.9	3.6
10.3	..	+ .03	1.3	2.0
20.0	0.6	− .3	0.8	1.3
11.2	.6	+ .6	.0	2.5
20.1	.6	− .5	.8	1.3
00.4	1.3	− .9	2.3	1.3

Reflections were indexed on the basis of a hexagonal unit cell with $a = 5.83 \pm 0.05$ Å., and $c = 9.33 \pm 0.05$ Å. The volume of the unit cell is 270 cu. Å.

The density of crystalline cyclopentane is not known from independent measurements, but a reasonable extrapolation from the density of the liquid (d_{20} 0.745) to that of the solid at −110°, indicates that there are two molecules per unit cell. (This implies a 13% change in density over this temperature range.)

Intensities of reflections dropped off rapidly with increasing Bragg angles; no reflections beyond $\theta = 20°$ were observed. Reflections of the type $(h, h, 2\bar{h}, l)$, were observed only for $l = 2n$; $(h, \bar{h}, 0, l)$ reflections were observed for l both odd and even. The most probable space groups are therefore

$$D_{6h}^{4}\ (C\tfrac{6}{m}mc),\ C_{6v}^{4}\ (C6mc)\ \text{and}\ D_{3h}^{4}\ (C\bar{6}2c)$$

The bimolecular unit cell and the c/a ratio of 1.60 indicate that the molecules are in hexagonal close-packed positions. Such positions are present in each of the three space groups.

Discussion.—It is evident that the intrinsic symmetry of cyclopentane molecules must be enhanced by rotational or orientational disorder in order that they may form the pattern units of bimolecular hexagonal unit cells. In computing structure factors for comparison with values of $F_{obs.}$ three types of molecular disorder, consistent with the crystal symmetry, have been considered: (a) molecules arranged in any one of 3 equivalent positions, 120° apart, rotated about a line parallel to the c axis; this line passes through the center and one carbon atom of individual molecules; (b) freely rotating (or randomly oriented)[7] molecules

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[1] This work has been supported by the Office of Naval Research.

[2] A quantity of purified cyclopentane and neohexane was furnished for this study by Dr. J. G. Aston of Pennsylvania State College.

[3] J. G. Aston, H. L. Fink and S. C. Schumann, This Journal, **65**, 341 (1943).

[4] J. E. Kilpatrick and K. S. Pitzer, *ibid.*, **68**, 1067 (1946).

[5] B. Post, R. S. Schwartz and I. Fankuchen, *Rev. Sci. Instr.*, **22**, 1218 (1951).

[6] J. M. Robertson, *ibid.*, **20**, 175 (1943).

[7] Freely (continuously) rotating molecules cannot be distinguished from randomly oriented molecules by the X-ray methods used in this investigation; both have the same symmetries on the average.

having cylindrical symmetry on the average, with the cylinder axis parallel to the c-axis; (c) freely rotating molecules having spherical symmetry on the average. The scattering factors, f_j, of atoms which, because of rotational motion, are considered to be uniformly distributed over some region, must be multiplied by correction terms which depend on the nature of the motion. For free spherical rotation, which results in the uniform distribution of atomic centers over the surfaces of spheres of radius r_j, the correction term[8] is of the form $\frac{\sin x}{x}$ where $x = \frac{2\pi r_j}{d_{hkl}}$ and d_{hkl} is the spacing of the plane whose scattering factor is being computed. The expression for the structure factor is then

$$F_{hkl} = \sum_j f_j \frac{\sin 2\pi \frac{r_j}{d_{hkl}}}{2\pi \frac{r_j}{d_{hkl}}} \exp 2\pi i \left(h\frac{u_j}{a} + k\frac{r_j}{b} + l\frac{w_j}{c}\right) \quad \text{(I)}$$

For free cylindrical rotation, where atomic centers are uniformly distributed on circles of radius "r," the correction term is

$$J_0\left(\frac{\pi 2 r_j}{d_{hkl}} \sin \psi\right)$$

where J_0 is the zero order Bessel coefficient and ψ is the angle between the axis of rotation and the normal to the plane (hkl).[8]

In so highly disordered a structure, intramolecular distances could not be determined from the X-ray diffraction data. Molecular dimensions, as determined by electron diffraction measurements,[9] were used in computing F_{hkl}.

Values of F_{calc} for each of the three types of disorder are listed in Table II together with values of F_{obs}.

It is seen that structure factors calculated on the assumption of freely rotating (or randomly oriented) molecules are the only ones giving good agreement with values of F_{obs}.

The minimum distance between the centers of carbon atoms of adjacent molecules is only 3.2 Å., probably resulting in some steric hindrance to free rotation. The X-ray and thermal data indicate, however, that this hindrance does not seriously impair the effectively spherical symmetry of individual molecules.

II. Neohexane (2,2-Dimethylbutane)

Experimental.—Optical examination showed a change from a birefringent crystal form below Transition II, to an isotropic form above the transition temperature. Oscillation diagrams were obtained of single crystals of this phase at −120 ± 5° rotating the crystal about the [100] axis.

The unit cell is face-centered cubic and contains four molecules; $a_0 = 8.90 \pm 0.05$ Å. Intensities of reflections decrease very rapidly with increasing Bragg angles. Reflections were observed only from the (111), (200), (220) and (222) planes; the first two were very strong; the latter two very weak.

Discussion.—The marked similarity between the thermal patterns of crystalline neohexane and cyclopentane is shown clearly in Table I. One difference may be noted: the molal heat capacity of neohexane, unlike that of cyclopentane, *increases* slightly at Transition II.

The asymmetric neohexane molecules must be highly disordered in order to crystallize in a face-centered cubic lattice with one molecule per lattice point. This high crystal symmetry and the extremely rapid decrease of intensity of reflections with Bragg angle suggest randomness of molecular orientations, probably with spherical symmetry on the average. In view of the fact that only four reflections were observed, a quantitative comparison of values of F_{calc} with F_{obs} does not appear to be justified. It may be noted, however, that the assumption of molecules randomly oriented about their centers of mass leads to values of F_{calc} in fair agreement with those observed.

BROOKLYN, N. Y.

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[8] W. H. Zachariasen, "Theory of X-Ray Diffraction in Crystals," John Wiley and Sons, Inc., New York, N. Y., 1945, p. 223.

[9] L. Pauling and L. O. Brockway, THIS JOURNAL, **59**, 1223 (1937).